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Effects of Constant-Current Reversals During Charge of the Silver Oxide Electrode

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ABSTRACT

The sintered silver electrodes used in storage batteries were charged by a constant current, interrupted by periodic constant-current discharge. A large capacity increase was obtained when the charge current was reversed for 15 min out of every 60 min during a charge at the 20-hr rate, but this method greatly increased the total time required for a charge. Capacity could be improved a smaller amount, without charge time becoming excessive, by partly discharging the silver electrodes the first one or two times that the potential reached a chosen value near the end of a charge. In general, capacity improvement decreased as KOH concentration increased. Commercial silver-zinc cells always gave less improvement than the test cells.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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EFFECTS OF CONSTANT-CURRENT REVERSALS DURING CHARGE OF THE SILVER OXIDE ELECTRODE

INTRODUCTION

Alkaline storage batteries containing silver oxide electrodes are used because of their high capacity compared to the more common storage battery systems. The discharge capacity of silver oxide electrodes is, however, strongly influenced by conditions of the preceding charge (anodic oxidation). Previous work at NRL has shown several ways for charging silver electrodes that will give a capacity greater than the capacity obtained by a constant-current charge. The electrode capacity can be increased if pulses of charge current are added to a constant-charging current, using the proper conditions (1). Either increased capacity or faster recharging can result from interrupting the current periodically throughout a charge (2). The largest improvements were obtained following charges with 60 cps asymmetric sinusoidal ac derived from commercial ac (3). This asymmetric ac was composed of two half-wave rectified currents which flowed in opposite directions and were 180 degrees out of phase. Capacity improvements were smaller when silver electrodes were charged by an asymmetric ac which was obtained by superimposing a half-wave 60 cps current in the discharge direction on a larger constant-charge current. The present report describes the results of relatively long constant-current reversals which were separated by long periods of constant-current charge.

EXPERIMENTAL PROCEDURE

Sintered silver plaques that were wrapped in cellulosic separator material were used for both the cathode and anode of the test cells. The plaques and separator had been manufactured for use in commercial silver-zinc storage batteries. The silver plaques were 41.5 mm wide, 38.0 mm high, and 0.8 mm thick. The sintered silver had an average weight of 5.8 g, not including the grid of expanded silver metal. The weight of sintered silver corresponds to a theoretical electrode capacity of 2.9 amp-hr. The test cells contained an excess of either 35% or 50% KOH as the electrolyte and contained an Ag/Ag_2O reference electrode. All work was done at $25 \pm 1°C$.

As in the previous work (1-3) the constant current which resulted in a complete charge or discharge lasting approximately 20 hr was arbitrarily taken as the standard, or normal, charge and discharge current. Before any charges with a periodically reversed current were tried, the test cells were charged and discharged for 8 to 10 complete cycles at the 20-hr current, until capacity became relatively constant. After the tenth cycle, the same current was used for the rest of the life of these cells, and corrections were not made for deviations in charge and discharge time from 20 hr.

Complete normal charges (using the 20-hr rate as defined above) were alternated with complete charges which used one of two reversal conditions. Under one set of conditions, the current was reversed periodically during a charge at the 20-hr rate, with the electrode being discharged at the 20-hr rate for 0.01 to 15 min during this reversal period before the charge was resumed. These reversals were repeated throughout the charge at intervals varying from 1 min to 4 hr, with only one reversal length and interval used in any single charge. In another set of reversal conditions, the electrode was partly discharged the first two times that charge potential reached a chosen value near the end

of a charge, with up to 5% of the electrode capacity being removed in each of the two partial discharges. All charges were continued until oxygen evolution was occurring and potential had stopped changing rapidly. After a charge was completed, a cell was immediately discharged at approximately the 20-hr rate of constant current to a final potential which was 300 mv negative to the Ag/Ag_2O reference. Charge and discharge currents were obtained from controlled power supplies.

To minimize variations in capacity the discharge capacities of the four normal cycles (20-hr constant-current charge and discharge) that were nearest each discharge were averaged. This moving average was then taken as the normal capacity at that particular point in the life of a cell and is the capacity referred to whenever normal capacity is mentioned. The capacity of each discharge was calculated as a percent of this varying average. Thus, the discharge capacity which followed a charge with current reversals could be compared to a value which was representative of actual cell capacity, regardless of changes in normal capacity over the life of a cell.

Some of the charges with current reversal and which resulted in increased test-cell capacity were tried with one model of a commercial silver-zinc secondary cell. Each commercial cell had four sintered silver electrodes of the same size as the test electrodes, had five zinc electrodes, and contained either 35% KOH or 45% KOH. The silver electrodes limited cell capacity and gave a theoretical cell capacity of about 11.5 amp-hr, although the nominal rated cell capacity given by the manufacturer was only 5 amp-hr. The silver-zinc cells were charged individually until cell potential reached 2.05 v. Complete charges at the 20-hr rate of constant current (as defined above) were alternated with charges which had current reversals. The cells were discharged at the 20-hr constant current to 1.10 v. Since capacity of these cells varied from one charge-discharge cycle to the next, the 20-hr current was recalculated after each constant-current cycle, and a different current was used for the following cycle whenever actual charge and discharge time had deviated greatly from 20 hr.

RESULTS

Current reversals that were repeated every 1, 10, or 30 min during a constant-current charge of a silver electrode had comparatively little effect on charge acceptance (Table 1). In contrast, the relatively long reversal time of 15 min had a strong effect on charge acceptance when the reversal was repeated every 60 min (Table 1). Since the reversal time of 15 min repeated every 60 min was effective for increasing capacity, this reversal was also tried with the commercial silver-zinc cells, but the average discharge capacity obtained with 35% KOH was 114% of the normal capacity and with 45% KOH it was only 95% of normal capacity (averages of two measurements).

In a modification to shorten the time required for a complete charge, the silver electrodes in the test cells were discharged at the 6-hr rate for 5 min after every 45 min of charge at the 20-hr rate in 35% KOH. Three complete charges gave an average capacity only 102% of normal. This contrasts with the 143% average given in Table 1 for the same quantity of reversal done at the 20-hr rate after every 45 min of charge.

Except for the charges with 15-min reversals, the charges listed in Table 1 had potentials that tended to resemble each other. Figure 1 gives excerpts from four charges having periodic current reversals lasting from 3 to 30 sec. This figure shows potentials during some of the brief reversals and potentials after charge was resumed. The five excerpts given on each part of Fig. 1 show potentials from approximately the same five periods during a charge. The earliest portion shows the first reversal after the charge began. The second portion shows potentials obtained near the end of the Ag/Ag_2O potential plateau of the charge, shortly before AgO began to form. The third portion shows potentials soon after the charge potential made the rapid rise to the Ag_2O/AgO potential

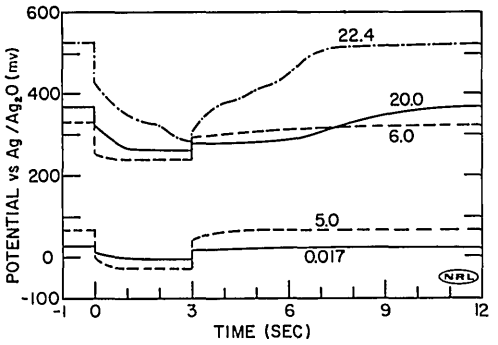
Table 1
Discharge Capacity of Silver Oxide Electrodes Following Charges with Periodic Current Reversal (Charge and discharge current were at the 20-hr rate)

Reversal Time		Reversal Repetition Period (min)	Average Discharge Capacity (% of normal capacity)	
Percent of Total Time	Minutes of Reversal		35% KOH	50% KOH
0.67	0.2	30	98 [3]*	—
1.0	0.01	1	102 [3]	—
1.7	0.5	30	97 [2]	100 [2]
2.0	0.2	10	99 [3]	—
3.3	1.0	30	99 [3]	—
5.0	0.05	1	94 [2]	—
5.0	0.5	10	111 [4]	99 [1]
6.25	15.0	240	95 [3]	—
8.33	15.0	180	105 [3]	—
10	1.0	10	87 [5]	—
10	3.0	30	89 [3]	98 [1]
12.5	15.0	120	92 [5]	102 [1]
16.7	15.0	90	109 [7]	92 [1]
20	0.2	1	97 [3]	—
20	2.0	10	101 [6]	98 [1]
25	15.0	60	143 [5]	77 [2]

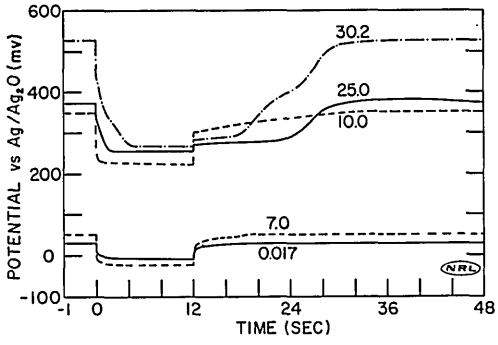
*Values in brackets give the number of measurements made.

plateau. The fourth portion shows potentials obtained near the end of the Ag_2O/AgO potential plateau. The final portion shown on Figs. 1a to 1d gives potentials after strong oxygen evolution was reached.

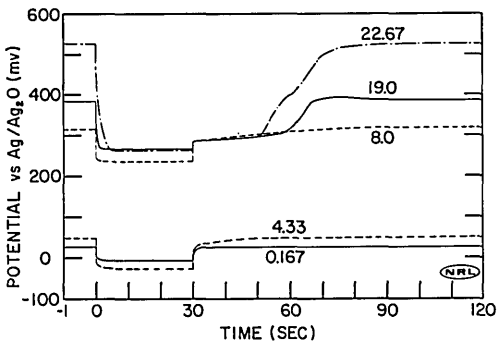
Figures 2 and 3 give excerpts of silver electrode potentials taken from two charges that had current reversed for 0.25 hr every 1.5 hr. As shown in Table 1, this charge procedure gave a discharge capacity in 35% KOH that averaged 109% of the normal capacity. There was, however, considerable variation in the seven individual capacities that were averaged to give 109%. Four of the seven charges that had 0.25-hr reversals every 1.5 hr gave discharge capacities from 95% to 98% of normal capacity, but the other



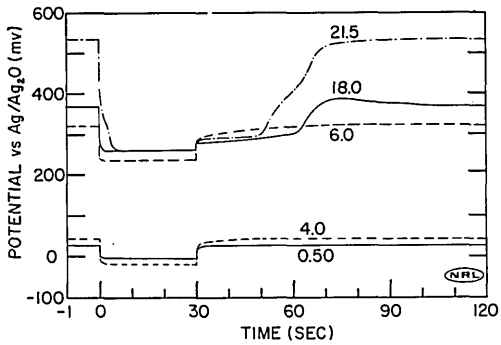
(a) Current reversal of 3 sec every 60 sec



(b) Current reversal of 12 sec every 60 sec



(c) Current reversal of 0.5 min every 10 min



(d) Current reversal of 0.5 min every 30 min

Fig. 1 - Some excerpts of potentials measured in 35% KOH during a constant-current charge of a silver electrode at the 20-hr rate. Numbers by the curves give the total elapsed time in hours at the end of reversals for each excerpt. The curves are given by different kinds of lines for clarity.

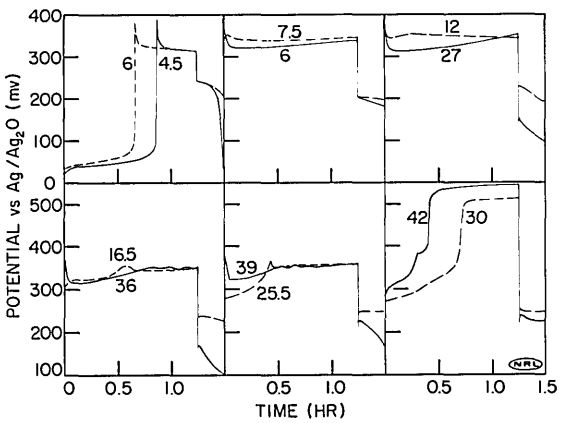


Fig. 2 - Some excerpts of potentials measured in 35% KOH during two constant current charges of a silver electrode at the 20-hr rate. Charge current was reversed for 0.25 hr every 1.5 hr. Numbers by the curves give the total elapsed time in hours at the beginning of each excerpt. Charges produced 133% of normal capacity (solid lines) and 95% (dashed lines).

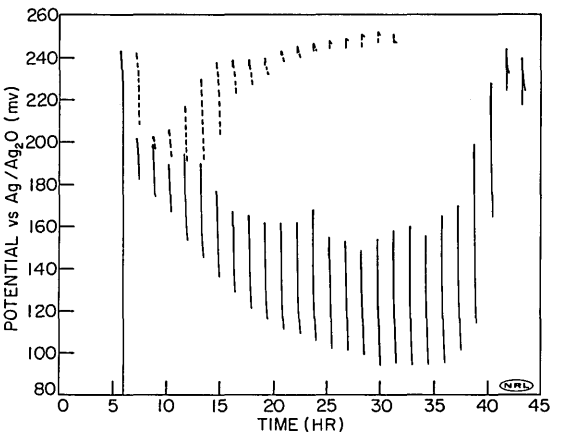


Fig. 3 - Reversal potentials during the two charges shown in Fig. 2. Solid lines give reversal potentials during the charge which produced 133% of normal capacity, and dashed lines give reversal potentials during the charge which produced 95%.

three charges gave 116%, 128%, and 133% of normal capacity. The discharges that gave 95% and 133% of normal capacity represented 58% and 79% of the capacity theoretically possible, respectively. The solid lines in Fig. 3 show that reversal potentials of a charge which gave improved capacity tended to be at successively lower values during the first half of a charge at the Ag_2O/AgO plateau (in contrast to reversals during a charge which gave normal capacity, shown by dashed lines), although the amount of AgO that was present on the electrode increased in this period. This resembles previous results when charge current was interrupted periodically throughout a charge (2). Under these conditions the open-circuit potentials also reached successively lower values as the amount of AgO present increased for half of a charge at the Ag_2O/AgO plateau.

A disadvantage of reversing charge current periodically under the conditions listed in Table 1 was that a complete charge required well over 20 hr. It seemed likely that reversal had more effect near the end of a charge than in the earlier part of a charge, judging by potential changes observed during and after reversals. If the number of reversals were lowered, the time required for a complete charge of the silver electrode would be decreased, because the time spent in reversal and the charge time spent in replacing the capacity removed during reversal would both be decreased. Therefore, a series of charges were done in which current was reversed the first two times that a given electrode potential was reached. The potentials chosen were 400, 440, 480, and 510 mv vs the Ag/Ag_2O reference electrode. These potentials were not reached until near the end of a charge.

Some of the results of partially discharging silver electrodes the first two times that a particular charge potential was reached are given in Table 2. After the capacity removed by the reversal was replaced, additional charge was accepted before charge potential again reached the reversal point. Table 2 is arranged according to the additional charge accepted after the first reversal. The additional charge time was a better measure of capacity than was the average discharge capacity, because normal capacity after a constant-current charge varied irregularly by several percent. Since charges were done at the 20-hr rate of constant current, each additional hour of charge gave approximately 5% additional capacity. Table 2 includes a few open-circuit stands for comparison, although stands were quite ineffective for increasing capacity under these conditions. There was no significant difference between the results when the reversal potential was 440, 480, or 510 mv; therefore, the results for these potentials are combined and summarized in Table 2. Only five charges were done with 400 mv as the reversal potential, because the additional charge accepted when using this reversal potential was only 70 to 80% of the additional charge accepted at 440 to 510 mv. The results with 400 mv are not included in Table 2. All reversal conditions listed in Table 2

Table 2
Effect of Reversing Current the First Two Times that Potential Reached a Particular Value During a Charge at the 20-hr Rate (Charge potential of silver oxide electrode at reversal point was 440, 480, or 510 mv vs Ag/Ag_2O)

Reversal Rate of Discharge (hr)	Reversal Time (min)	Capacity Removed by Reversal (% of normal)	Average Additional Charge Time (hr)*		Average Discharge Capacity after Charge Completion (% of normal)
			After First Reversal	After Second Reversal	
20	30	2.50	3.18	0.31	116 [9]†
20	60	5.00	2.72	0.34	115 [4]
10	30	5.00	2.71	0.27	114 [4]
10	15	2.50	2.28	0.27	111 [7]
5	15	5.00	2.26	0.26	113 [4]
20	15	1.25	2.22	0.26	110 [6]
40	60	2.50	2.16	0.26	113 [4]
80	60	1.25	1.25	0.20	109 [4]
6.7	5	1.25	0.96	0.18	106 [7]
20	6	0.50	0.66	0.11	103 [5]
80	15	0.31	0.54	0.11	103 [4]
2	1.5	1.25	0.47	0.12	102 [7]
‡	30	0.0	0.34	0.07	103 [3]
‡	15	0.0	0.23	0.05	103 [3]
20	30	2.50	0.22§	0.07§	102 [4]
‡	15	0.0	0.07§	0.03§	104 [3]

*Average time required for the reversal point to be recovered after replacing the capacity that was removed during the brief reversal.
†Values in brackets give the number of measurements made.
‡Open-circuit stand.
§In 50% KOH solution. All others were done in 35% KOH solution.

resulted in increased capacity, although the increase was very small under some conditions. A second reversal at the same potential during one charge gave much less additional charge acceptance than was obtained after the first reversal. The few times that a third reversal was done at the same potential, added charge was less than it had been after the second reversal.

The effect of two 30-min reversals at the 20-hr rate was tried with the commercial silver-zinc cells. The additional charge time in 35% KOH averaged 0.54 hr and 0.15 hr after the first and second reversals, respectively. These values were much less than

the values obtained with the test cells in 35% KOH (top line of Table 2). For the commercial silver-zinc cells containing 45% KOH, the additional charge averaged 0.21 and 0.08 hr after the first and second reversal, respectively.

DISCUSSION

The results obtained with relatively long reversals using a constant current (Table 1) were, in general, markedly inferior to the results when the reverse current was derived from 60 cps asymmetric ac (3). No increase in capacity was obtained under most of the conditions that were tried. The only consistent and large increase came after a charge in which current was reversed for 15 out of every 60 min. This charge gave a capacity averaging 143% of the normal capacity, a value very close to the maximum capacity obtained following a charge in which current was held constant for long periods and then was increased for a few seconds (1). Approximately the same capacity was obtained when the electrode was charged by a rapidly pulsating unidirectional current (2), but a larger capacity could be obtained following a charge with 60 cps asymmetric ac (3).

Although a large capacity was obtained by reversing the charge current for 15 out of every 60 min, a disadvantage to using long reversals was that the time required for a complete charge always exceeded 20 hr because of the necessity to replace the capacity removed during each reversal. Time could be shortened by having long charge periods between the reversal periods, but then it often happened that no reversal occurred near the end of a charge, at the point where a reversal seemed most effective for increasing capacity. Although long reversals were the most beneficial reversals, not many charges with repeated discharges were tried in which over 1% of the capacity was removed with each reversal, because time required for a complete charge became excessive. When the 20-hr charge current was used with current reversed for 15 out of every 60 min, 40 hr were required before a cell had a net charge of even 100% of normal capacity, and nearly 2.5 days were required for a complete charge. It should be noted, however, that the capacity averaging 143% of normal capacity obtained with this charge-discharge parameter was much larger than the 112% of normal capacity obtained after an electrode was charged using a steady constant current at the 2.5-day rate.

If maximum capacity is desired and total charge time is relatively unimportant, this charge with long reversals is preferable to a charge at a low constant current. If a constant discharge potential is desired, a low rate of constant charge current or the asymmetric ac (3) may be preferable. An electrode charged at a low current has less surface area than an electrode charged at a high current (4). The initial potential plateau during discharge of an electrode with small surface area is at a relatively low potential, because AgO on the surface is rapidly covered by Ag_2O during discharge, judging by the results of x-ray diffraction (4); most of the discharge takes place at the Ag_2O/Ag potential even though part of the current still is produced by the reduction of AgO. A low charge rate is preferable if the electrolyte concentration is high, for example 45% or 50% KOH. As charge current density increases, i.e., charge time decreases, capacity falls more rapidly in concentrated KOH than in more dilute KOH. For example, when the commercial silver-zinc cells were charged at the 40-hr rate, a cell containing 45% KOH gave about 112% of normal (20-hr) capacity, while a cell containing 35% KOH gave only 105% of normal capacity.

Normal charge acceptance of a silver oxide electrode could be increased 15%, without charge time becoming excessive, by partially discharging the electrode once or twice near the end of a charge (Table 2). The second reversal was not worth attempting unless a large amount of charge had been accepted after the first reversal. The additional charge after a second reversal was usually only 10 to 25% of the charge added after the first reversal. Effectiveness of the reversals generally correlated with the amount of capacity removed. To obtain a capacity improvement that exceeded 10%, the capacity

removed during each reversal had to be over 1% of the normal electrode capacity. This result correlated with results found when reversals were repeated periodically throughout a charge (Table 1). For a specific amount of reversal near the end of a charge, the rate of reversal current was also an important factor (Table 2). Another important factor was electrolyte concentration. Although the added capacity was small under many of the conditions used, the recharge did always exceed the capacity removed during each of the two partial discharges.

Reports differ as to whether porous silver electrodes react first at the conducting grid or at the electrode surface. Romanov (5) used pressed-silver-powder electrodes and reported that the oxides were concentrated at the grid after a direct current charge. Dirkse (6,7) reported that pellets of pressed Ag_2O or AgO gave the potential of material next to the grid and not the potential of the bulk composition of the pellets. These results, when pressed materials were used, contrast with results obtained by x-ray diffraction of sintered silver electrodes (8) and roughened sheet silver (4). Here the potentials were determined by the material on the surface, and oxidation of Ag_2O and reduction of AgO took place initially on the surface of the electrode next to the solution. The newly formed oxide could be detected when it was present in a smaller amount than was necessary for detecting one component of a mixture by x-ray diffraction. This indicated that when Ag_2O was oxidized or AgO was reduced the initial formation must have been concentrated on the electrode surface. The initial formation of Ag_2O on Ag was not detected as readily by x-ray diffraction, because the initial oxidation occurred on the surface of silver particles, which were distributed throughout the electrode. Similarly, x-ray diffraction showed that when Ag_2O was reduced, relatively little Ag formed on the surface at first.

Microscopic examination of sintered silver electrodes has confirmed that the reactions are not concentrated at the grids. Microscopic examination of electrodes in various states of discharge indicated that Ag_2O and Ag did not tend to form first at the grids and be concentrated there (9) and that Ag_2O and AgO did not tend to form first at the grids during a constant-current charge (10). A large amount of unoxidized silver was still present in the vicinity of the grids at the end of a charge. Higher electrical resistance in some unsintered pressed powders may be the cause for the different behaviors that have been reported in the literature. All reactions may take place at the conducting grid with some pressed-powder electrodes merely because there is less IR drop near the grid of these electrodes than there is at the electrode surface.

A large part of the silver had been oxidized to AgO by the time a normal charge of a sintered silver electrode ended, although substantial amounts of metallic silver remained, as well as thin coatings of Ag_2O on this Ag (9,10). Much of the surface and many internal cavities were partially or completely filled with AgO crystals. When a nearly charged electrode was discharged briefly under the conditions in Table 2, part of the AgO was converted to Ag_2O. This reduction may have exposed some areas of the Ag_2O-coated Ag that had been tightly covered by AgO crystals. AgO tends to form into much larger crystals than does Ag_2O. Significant changes in crystal size and shape occur as the silver oxides are reduced or silver is oxidized (9,10). Although the change in total volume is only slight as AgO is reduced to Ag_2O, the crystal lattice is distorted as dimensions change in going from monoclinic to face-centered cubic crystals. Lattice dimensions indicate that a large expansion of the crystal occurs as metallic silver is oxidized to Ag_2O, and recent coulogravimetric measurements have confirmed that a large volume change occurs (11).

When a charge was resumed after a reversal near the end of a charge, current may have been divided between oxidizing the Ag_2O formed during the reversal and oxidizing Ag_2O-coated Ag that had been exposed where openings had formed in the AgO coating. A long reversal, during which relatively large amounts of AgO were reduced, probably exposed larger areas of Ag_2O-coated Ag than were exposed after short reversals. The

excess of charge capacity over reversal capacity was, therefore, significantly larger after a long reversal than after a short reversal (Table 2). Much of the current during a second reversal would probably reduce the same areas of AgO that were reduced after the first reversal. A second reversal was, therefore, much less effective than the first reversal in exposing silver and promoting formation of additional AgO after the charge was resumed.

Although most of the periodic reversals repeated throughout a charge were not effective for increasing total charge capacity (Table 1), the charges were of some interest because of the potentials observed. The potentials shown in Fig. 1 are generally similar, despite conditions which varied from 3 to 30 sec for reversal length, from 1 to 30 min for reversal repetition frequency, and from 1.7 to 20% for amount of time on reversal. During the early portion of the Ag_2O/AgO potential plateau, charge potential rose gradually after a reversal until a potential was reached which slightly exceeded the value measured just before reversal, and then potential slowly fell (Fig. 1). Later in the Ag_2O/AgO plateau the charge potential developed two steps after each brief reversal. During the first step the electrode charged at a potential only slightly above the Ag_2O/AgO equilibrium* until approximately 100% of the capacity lost during reversal had been replaced. Probably almost all current was oxidizing Ag_2O that had formed at readily accessible sites during the reversal. Then the reaction shifted to oxidation of sites which required more energy. Potential rose rapidly, passed through a maximum, and decreased slowly until a steady charging potential was reached again.

When current was reversed for 0.25 hr every 1.5 hr, the potential pattern obtained from the silver electrode during charges which gave improved capacity differed from the pattern during charges which gave normal capacity. During the charges which gave improved capacity, there was a potential maximum when charge current was resumed following each reversal at the Ag_2O/AgO potential plateau, except the final reversal before reaching oxygen evolution (solid lines in Fig. 2). Following these initial maxima, potentials fell to relatively low values during charges having improved capacity. There were only one or two such maxima during charges that gave normal capacity (dashed lines in Fig. 2). During charges that gave normal capacity the potential of silver electrodes tended to have successively lower values as charge was resumed after each reversal. Charges having the highest capacity had low reversal potentials during most of the charge (Fig. 3) and high gas evolution potentials at the end of a charge (Fig. 2). A charge that gave the intermediate capacity of 116% had most reversal potentials in the range from 215 to 195 mv, intermediate between the two sets of values shown in Fig. 3. Thus, the relative discharge capacity that was going to be obtained could be predicted before this type of charge was half completed.

These potential changes during charges with relatively long reversals gave an indication of possible electrode conditions. After Ag_2O had started to oxidize to AgO, the first reversal began at a potential close to the AgO/Ag_2O equilibrium (Figs. 2 and 3). At this time the electrode contained relatively large amounts of Ag_2O and Ag, with a small amount of AgO present on the surface (4). Then, in the charges which gave improved capacity, came a series of reversals in which potentials were successively lower, although increasing amounts of AgO were present on the electrode. Microscopic examination of electrodes during constant-current charges indicated that all areas do not react simultaneously (10). AgO may form in one area, while it has not in an adjacent area. In charges with reversals which resulted in improved capacity, the AgO may have had a tendency to form a tighter coating or a thicker coating that blocked electrolyte channels more than usual and hindered ion movements. The successively lower discharge potentials probably resulted from a progressive hinderance to the reduction of AgO as the

*The equilibrium potential of the Ag_2O/AgO couple vs Ag/Ag_2O has been given as 261 mv (7) and as 262 mv (12).

amount of AgO increased. The unusually low potentials during reversal were followed by charge potentials that began at a high value. Since the same amount of Ag_2O was produced during the reversal periods of both charges shown in Fig. 2, it was unlikely that the potential maxima upon resuming charge were due to resistance of Ag_2O.

A change must then have occurred in the charges which gave improved capacity. Perhaps formation of AgO was initiated at new sites by the high potentials, or perhaps oxygen from the surface layers could penetrate deeper into the oxide layer under the influence of a high charging potential and could oxidize additional silver. When charge potential reached a maximum and then decreased, possibly the potential fall resulted from decreasing local current densities as AgO began to form in a larger number of sites, or possibly a blocking AgO coating cracked as a result of expansion as oxides formed below the AgO surface. Increased porosity would allow the electrolyte to penetrate nearer to the metallic silver that remained and result in decreased concentration gradients in the AgO layer. Charge potential fell to a value close to equilibrium values, lower than the potential of normal charges. Although the exact nature of the process is unknown, it apparently took place repeatedly and allowed more AgO than usual to be formed before diffusion through the AgO became sufficiently difficult that electrode potential rose to the oxygen evolution value. The few charges with periodic long reversals which resulted in improved capacity (Table 1) may have had charge and reversal periods proportioned correctly to give a potential maximum each time that charge was resumed.

After the initial potential maximum when charge was resumed, the charges which gave improved capacity often had additional smaller maxima as gradually rising potentials reached 351 to 355 mv (Fig. 2). Potentials dropped 4 to 10 mv after reaching the maxima and then again increased gradually. Many more of these slow potential fluctuations occurred in charges that gave the high capacity than in other charges. Charges at the 20-hr rate which gave normal capacity usually exceeded 355 mv only when potential made the sharp rise from the Ag/Ag_2O plateau to the Ag_2O/AgO plateau and again as potential rose slowly near the end of a charge (Fig. 1).

The differences between results with the commercial silver-zinc cells and the test cells were probably due mainly to different concentration gradients. It is doubtful that the presence or absence of zinc was important. The commercial cells were tightly packed and had a limited amount of free electrolyte. This arrangement should result in concentration gradients near the electrode surface being larger in the commercial cells than they were in the test cells at the same current density. Therefore, the commercial cells showed less improvement after a charge with reversals than the test cells.

SUMMARY

During charges of the sintered silver electrodes used in storage batteries, in one set of conditions periods of constant-current charge were separated by shorter periods of constant-current discharge. Current reversals lasting 0.01 to 3 min repeated every 1 to 30 min at the 20-hr rate had little effect on charge acceptance. Reversals of 15 min repeated every 60 min during a charge at the 20-hr rate increased capacity of test cells by an average of 43% in 35% KOH but had the disadvantage of greatly increasing the total time required for a charge. Capacity was, however, much larger than the capacity obtained from an uninterrupted constant-current charge requiring the same total time. More widely separated reversals of 15 min gave less improvement. Reversals seemed most effective for increasing capacity when they occurred near the end of a charge.

In another set of conditions, the sintered silver electrodes were partly discharged the first two times that charge potential reached a chosen value near the end of a charge. Average capacity of test cells was improved by up to 16% without charge time becoming excessive. Effectiveness of reversals near the end of a charge correlated with the

amount of capacity removed and was also affected by the rate of the reversal current. The second reversal gave much less added capacity than the first reversal gave.

In general, as KOH concentration increased, capacity improvement decreased. Commercial silver-zinc cells always gave less increase in capacity than the test cells gave.

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13. ABSTRACT

The sintered silver electrodes used in storage batteries were charged by a constant current, interrupted by periodic constant-current discharge. A large capacity increase was obtained when the charge current was reversed for 15 min out of every 60 min during a charge at the 20-hr rate, but this method greatly increased the total time required for a charge. Capacity could be improved a smaller amount, without charge time becoming excessive, by partly discharging the silver electrodes the first one or two times that the potential reached a chosen value near the end of a charge. In general, capacity improvement decreased as KOH concentration increased. Commercial silver-zinc cells always gave less improvement than the test cells.

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